

Lecture 10

The Dispersion Force and van der Waals Interaction

In Lecture 9, we have seen the interactions caused by charges and dipoles, including the Keesom and Debye interactions that contribute to the r^{-6} vdW energy. In this lecture, we will discuss the last contribution to the vdW interactions, the London dispersion energy.

10.1 Classical view of dispersion interactions

From last lecture we have seen, that a term containing the electronic polarizabilities $\alpha_{0,i}$ of both molecules occurs as the result of unification of the polarization interactions. If we ignore any charge and dipole components, the interactions between neutral molecules still exist!

This type of energy, known as the “dispersion interaction”, has a non-trivial origin which stems from quantum electrodynamics. We can however, use a semi-classical method to approach it. Consider a Bohr atom with radius a_0 which has a transient dipole $u = ea_0$, if a neutral molecule is in its vicinity, it can be polarized by the field of the Bohr atom (Figure 10.1).

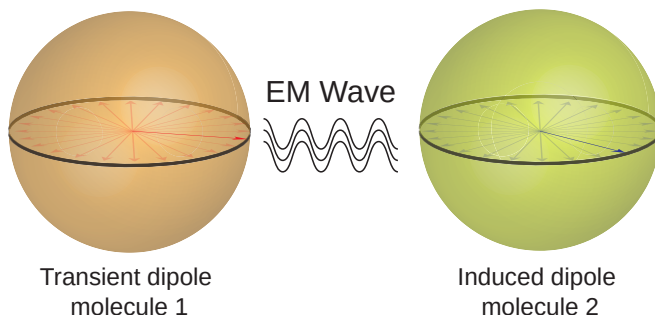


Figure 10.1: The dispersion force between 2 Bohr atoms can be seen as the electromagnetic wave between the transient dipole moments.

The interaction *free* energy is thus:

$$w_{\alpha\alpha}(r) = -\frac{(ea_0)^2\alpha_{02}}{(4\pi\epsilon_0\epsilon_r)^2r^6} \quad (10.1)$$

From the last lecture we know that, the electronic polarizability of Bohr atom with radius a_0 is $\alpha_0 = 4\pi\epsilon_0\epsilon_r a_0^3$:

$$\begin{aligned} w_{\alpha\alpha}(r) &= -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0\epsilon_r)r^6} \\ &= -2h\nu_1 \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0\epsilon_r)r^6} \end{aligned} \quad (10.2)$$

where $h\nu_1 = 13.6$ eV is the **ionization energy** of the Bohr atom, and *half* the Coulomb energy of a Bohr atom.

This is almost the correct result. The exact form of the London (free) dispersion energy is given by:¹

$$w_{\alpha\alpha} = -\frac{3}{2} \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0\epsilon_r)^2r^6} \frac{h\nu_{11}\nu_{12}}{\nu_{11} + \nu_{12}} \quad (10.3)$$

where $h\nu_{11}$ and $h\nu_{12}$ are the ionization energies of molecules 1 and 2, respectively. If $\nu_{11} = \nu_{12}$, this is only different from Equation 10.2 by a pre-factor.

But we immediately notice that such energy is proportional to $h\nu_1$ of both molecules, which is of the magnitude of 10 eV. On the other hand, the mathematical derivation from last lecture shows that the prefactor is proportional to $k_B T$. There is a difference by 2 orders of magnitude! This feature is explained by the frequency-dependent polarizability which we will cover later. Nevertheless, let's first take the result from the London dispersion theory, to complete our story of vdW interactions. With the Keesom, Debye and London interactions as individual recipes, we can build the complete form of the vdW interaction, written in free energy:

$$\begin{aligned} w_{\text{vdW}} &= -\underbrace{\frac{u_1^2 u_2^2}{3k_B T (4\pi\epsilon_0\epsilon_r)^2 r^6}}_{\text{Keesom}} - \underbrace{\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{(4\pi\epsilon_0\epsilon_r)^2 r^6}}_{\text{Debye}} - \underbrace{\frac{3\alpha_{02}\alpha_{01} \frac{h\nu_1\nu_2}{\nu_1+\nu_2}}{2(4\pi\epsilon_0\epsilon_r)^2 r^6}}_{\text{London}} \\ &= -\frac{\beta_{\text{Keesom}} + \beta_{\text{Debye}} + \beta_{\text{London}}}{r^6} \end{aligned} \quad (10.4)$$

We can see the coefficient β associated with the r^{-6} of Lenard-Jones potential is split into three contributions. Let's see some key features of the vdW interaction:

The London dispersion force is not weak at all.

Thanks to the relatively large ionization energies of atoms (~ 10 eV), the London dispersion is not weak. We can actually use the London dispersion energy to estimate the phase transition point of noble gases. Assume that in a noble gas liquid, the closest distance between two sphere-like atoms, is just the atom diameter σ . At the melting point (T_m) of the noble

gas liquid, the thermal kinetic energy $3/2k_B T_m$ overcomes the London dispersion energy, such that:

$$w_{\text{vdW}} + E_{\text{kin}} = -\frac{3\alpha_0^2}{4(4\pi\epsilon_0)^2\sigma^6} h\nu_I + \frac{3}{2}k_B T_m = 0 \quad (10.5)$$

where T_B is the melting point of the noble gas. We can see that this rough theory actually captures the experimental boiling point, such as:¹

- Ne: $\sigma = 3.08 \text{ \AA}$, $h\nu_I = 21.6 \text{ eV}$, $\alpha_0/4\pi\epsilon_0 = 0.39 \times 10^{-30} \text{ m}^3 \rightarrow T_m = 22 \text{ K}$. Experimental $T_m = 27 \text{ K}$
- Ar: $\sigma = 3.76 \text{ \AA}$, $h\nu_I = 15.8 \text{ eV}$, $\alpha_0/4\pi\epsilon_0 = 1.63 \times 10^{-30} \text{ m}^3 \rightarrow T_m = 85 \text{ K}$. Experimental $T_m = 87 \text{ K}$

The London dispersion force is dominating the vdW interaction between non-polar molecules.

This is easy to observe. In neutral or less-polar molecules the u is usually small and α is large.

Dipole-Dipole interaction becomes more important between highly polar molecules.

In highly polar molecular systems, such as interaction in water, the dipole interactions can be quite appreciable. This can be seen from the contribution of dispersion energy in total vdW interaction (gas phase).

- $\text{CH}_4 - \text{CH}_4$, $\beta_{\text{vdW}} = 102 \times 10^{-79} \text{ J} \cdot \text{m}^6$, $\eta_{\text{London}} = 100\%$
- $\text{HCl} - \text{HCl}$, $\beta_{\text{vdW}} = 123 \times 10^{-79} \text{ J} \cdot \text{m}^6$, $\eta_{\text{London}} = 86\%$
- $\text{NH}_3 - \text{NH}_3$, $\beta_{\text{vdW}} = 111 \times 10^{-79} \text{ J} \cdot \text{m}^6$, $\eta_{\text{London}} = 57\%$
- $\text{H}_2\text{O} - \text{H}_2\text{O}$, $\beta_{\text{vdW}} = 139 \times 10^{-79} \text{ J} \cdot \text{m}^6$, $\eta_{\text{London}} = 24\%$

Revisiting the relation $A_{AB} = \sqrt{A_{AA}A_{BB}}$

In lecture 1 we have seen the empirical equation that the Hamaker constant between 2 surfaces can be written as $A_{AB} = \sqrt{A_{AA}A_{BB}}$, when is it valid?

This is only applicable for situations where dispersion interaction dominates. We know that the vdW coefficient (the one associated with r^{-6}) $\beta_{AA} \propto \alpha_{0,A}^2 h\nu_A$ and $\beta_{BB} \propto \alpha_{0,B}^2 h\nu_B$, by taking that $h\nu_A \nu_B / (\nu_A + \nu_B) \approx \sqrt{h^2 \nu_A \nu_B / 2}$, we have $\beta_{AB} \approx \sqrt{\beta_{AA} \beta_{BB}}$. This assumption will break when contribution from permanent dipoles becomes more important, e.g. the interaction involving water.

The above analysis is also true for Hamaker constant $A_{AB} = \pi^2 \rho_A \rho_B \beta_{AB}$, when the London dispersion force dominates. Since $\rho_A \rho_B = \sqrt{\rho_A^2 \rho_B^2}$, we can instantly get $A_{AB} = \sqrt{A_{AA} A_{BB}}$.

10.2 Frequency-dependent dielectric response

The main reason why the London dispersion energy is related with $h\nu_I$ instead of $k_B T$, is that the interaction between induced dipoles are coming from the fluctuation of the EM waves and is frequency-dependent. The frequency-dependent electronic polarizability can be described by the Lorentz oscillator model (Figure 10.2).

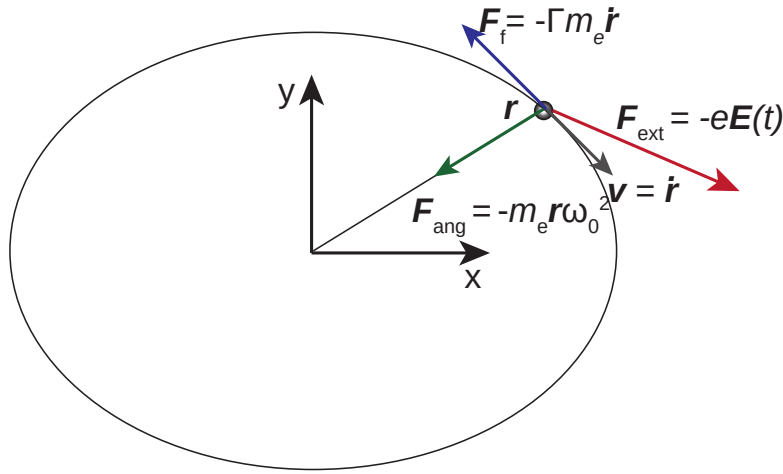


Figure 10.2: The forces on an electron in the classical Lorentz model.

We model the motion of an electron in a Bohr atom orbiting the nucleus. The Bohr atom has transient position $\mathbf{r}(t)$ with intrinsic oscillating frequency ω_0 . When external field $E(t)$ is interacting on the electron, the total force on the electron is $\mathbf{F}_{\text{tot}} = m_e \ddot{\mathbf{r}}$, which is contributed by:

- The external force: $\mathbf{F}_{\text{ext}} = -e\mathbf{E}$
- The angular force: $\mathbf{F}_{\text{ang}} = -m_e \mathbf{r} \omega_0^2$
- The friction (damping) force: $\mathbf{F}_f = -\Gamma m_e \dot{\mathbf{r}}$

The equation of motion is then written as:

$$m_e \ddot{\mathbf{r}} + \Gamma m_e \dot{\mathbf{r}} + m_e \omega_0^2 \mathbf{r} = -e\mathbf{E} \quad (10.6)$$

We can perform a Fourier transformation to \mathbf{r} and E from time domain to frequency domain:

$$\hat{\mathbf{r}}(\omega) = \int_{-\infty}^{\infty} \mathbf{r}(t)e^{-i\omega t} dt \quad (10.7)$$

$$\hat{\mathbf{E}}(\omega) = \int_{-\infty}^{\infty} \mathbf{E}(t)e^{-i\omega t} dt \quad (10.8)$$

and its reverse transformation looks like:

$$\mathbf{r}(t) = \int_{-\infty}^{\infty} \hat{\mathbf{r}}(\omega)e^{i\omega t} d\omega \quad (10.9)$$

$$\mathbf{E}(t) = \int_{-\infty}^{\infty} \hat{\mathbf{E}}(\omega)e^{i\omega t} d\omega \quad (10.10)$$

The derivatives of \mathbf{r} regarding t using Fourier transformation can thus be written as:

$$\dot{\mathbf{r}}(t) = \int_{-\infty}^{\infty} i\omega \hat{\mathbf{r}}(\omega)e^{i\omega t} d\omega \quad (10.11)$$

$$\ddot{\mathbf{r}}(t) = \int_{-\infty}^{\infty} -\omega^2 \hat{\mathbf{r}}(\omega)e^{i\omega t} d\omega \quad (10.12)$$

$$(10.13)$$

compare the left and right hand terms in the integral and finally we get:

$$m_e \hat{\mathbf{r}}(\omega)(-\omega^2 + i\Gamma\omega + \omega_0^2) = -e\hat{\mathbf{E}} \quad (10.14)$$

We can get the frequency ω -dependent electronic polarizability:

$$\alpha(\omega) = \frac{-e\hat{\mathbf{r}}(\omega)}{\hat{\mathbf{E}}(\omega)} = \frac{e^2}{m_e(\omega_0^2 + i\omega\Gamma - \omega^2)} \quad (10.15)$$

At zero frequency, we have $\alpha_0 = \alpha(\omega = 0) = e^2/(m_e\omega_0^2)$. We can also rewrite $\alpha(\omega)$ using α_0 :

$$\alpha(\omega) = \frac{\alpha_0}{1 + i\Gamma\frac{\omega}{\omega_0} - (\frac{\omega}{\omega_0})^2} \quad (10.16)$$

Note $\hbar\omega_0 = h\nu_1$ actually equals the ionization energy of an electron, we may also rewrite it in terms of ν :

$$\alpha(\nu) = \frac{\alpha_0}{1 + i\Gamma\frac{\nu}{\nu_1} - (\frac{\nu}{\nu_1})^2} \quad (10.17)$$

The frequency-dependent polarizability is a *complex* quantity, with its real part representing the phase and imaginary part representing the absorption of energy at frequency ω . The real part of polarizability approaches its maximum at ω_0 , as the electron is at resonance. To convert $\alpha(\nu)$ to a **real** function, we can use the *imaginary frequency* $i\nu$ as the variable, which gives:

$$\alpha(i\nu) = \frac{\alpha_0}{1 + \Gamma \frac{i\nu}{\nu_1} + \left(\frac{i\nu}{\nu_1}\right)^2} \quad (10.18)$$

The plot of $\alpha(\nu)$ and $\alpha(i\nu)$ can be seen in Figure 10.3. The polarizability in imaginary frequency is a monotonically decaying function, and is crucial for the calculation of vdW interactions. For molecules with multiple ionic absorption frequencies, it is more practical to sum all the polarizability to approach the exact solution, which improves the original London theory.

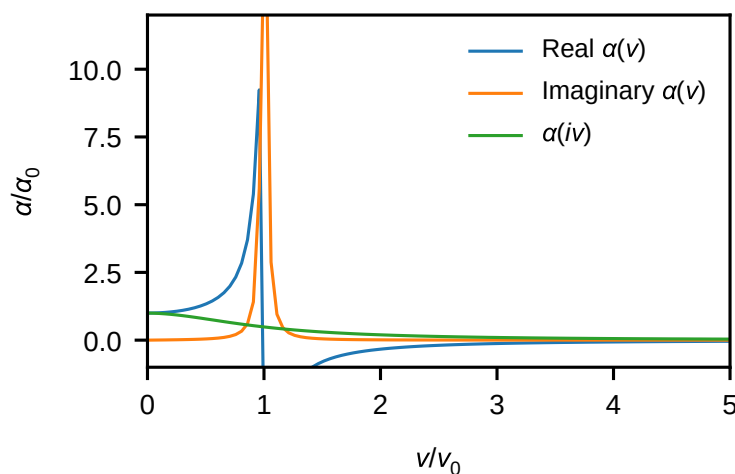


Figure 10.3: Typical plots of $\text{Re}(\alpha(\nu))$, $\text{Im}(\alpha(\nu))$ and $\alpha(i\nu)$, $\Gamma = 0.05$

Similar to the microscopic polarizability, the permittivity of a macroscopic material is also frequency-dependent. This can be seen using a simple capacitor model, as shown in Figure 10.4 left. Under an oscillating electric field (such as that in an AC circuit), the induced dipoles are not in phase with the external field, and the permittivity (known as the “dielectric function” in this case) varies with frequency ω . Typical real and imaginary dielectric functions of a medium, are shown in Figure 10.4 right.

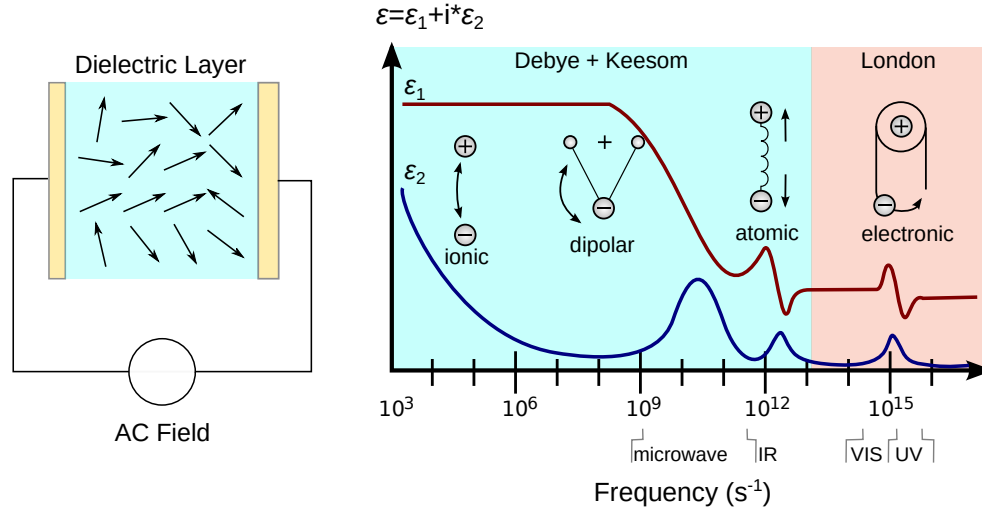


Figure 10.4: Frequency-dependent dielectric response. Left: polarization in a parallel-plate capacitor under AC field. Right: real and imaginary part of the dielectric function $\epsilon(\omega)$ of a medium as a function of ω .

10.3 Microscopic picture: McLachlan model

Microscopic: McLachlan model

The first complete theory for the vdW interaction involving 2 atoms in a medium, is proposed by McLachlan,² which is expressed as:

$$w_{\text{vdW}}(r) = -\frac{6k_{\text{B}}T}{(4\pi\epsilon_0)^2 r^6} \sum'_{n=0} \frac{\alpha_1(i\nu_n)\alpha_2(i\nu_n)}{\epsilon_3^2(i\nu_n)} \quad (10.19)$$

The \sum' notation means that the first term in the summation is multiplied by 1/2. The frequencies are sampled, only at discrete values that $h\nu_n = 2\pi k_{\text{B}}Tn$ (known as the Matsubara frequencies). The typical $\alpha(i\nu) - \nu$ plots of polar and non-polar molecules using the Lorentz model can be seen in Figure 10.5.

Equation 10.19 might seem complicated, but we can study two extreme cases:

1. Zero-frequency contributions

At zero frequency, we know from Lecture 9 that the polarizability reduces to the form of $\alpha_0 + u^2/(3k_{\text{B}}T)$, thus we have:

$$\begin{aligned} w_{\text{vdW}}(\nu = 0, r) &= -\frac{1}{2} \frac{6k_{\text{B}}T(\alpha_{01} + u_1^2/(3k_{\text{B}}T))(\alpha_{02} + u_2^2/(3k_{\text{B}}T))}{(4\pi\epsilon_0\epsilon_3^2)^2 r^6} \\ &= -\underbrace{\frac{u_1^2 u_2^2}{3k_{\text{B}}T(4\pi\epsilon_0\epsilon_3)^2 r^6}}_{\text{Keesom}} - \underbrace{\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{(4\pi\epsilon_0\epsilon_3)^2 r^6}}_{\text{Debye}} - \underbrace{\frac{3k_{\text{B}}T \alpha_{01} \alpha_{02}}{(4\pi\epsilon_0\epsilon_3)^2 r^6}}_{\text{London}(n=0)} \end{aligned} \quad (10.20)$$

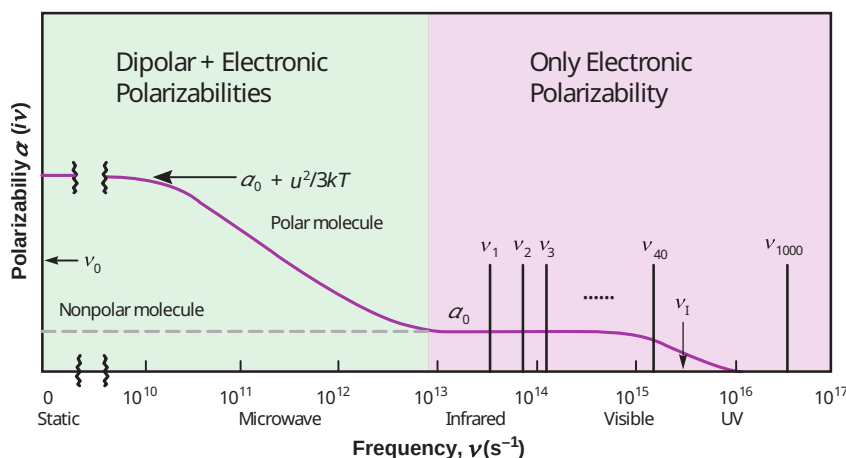


Figure 10.5: Typical molecular polarizability $\alpha(i\nu)$ as a function of ν for polar and non-polar molecules. The sampling frequencies at 300 K are shown as vertical lines. The dipolar polarizability has contribution only at zero frequency, since ν_1 is already in the optical range. Figure adapted from Israelachvili, *Intermolecular and surface forces* (Academic press, 2011).

We immediately see the recovery of the Keesom and Debye energies, as well as the $\alpha_{01}\alpha_{02}$ term from mathematical derivation. In fact, the last part is the zero-frequency part of the dispersion energy. Comparing the magnitudes of $k_B T$ and $h\nu$, we can see that the zero-frequency contribution to the dispersion energy is negligible.

2. Optical-frequency contributions

The lowest legal frequency $h\nu_1 = 2\pi k_B T \approx 0.16$ eV, is already in the IR range (Figure 10.5). The permanent dipoles cannot respond to such high frequency, therefore the dipole polarizability has no effect on the dispersion energy at optical frequencies. The electronic polarizability govern the dispersion energy at such frequencies. We first consider $\epsilon_3 = 1$, that the 2 molecules are in vacuum.

The summation in Equation 10.19 can be estimated using continuous integral at optical frequencies, if temperature is very low. Since $h d\nu = 2\pi k_B T dn$, we can rewrite the integral from $n = 1$ to:

$$w_{\text{vdW}}(\nu > 0) = \frac{h}{2\pi} \frac{6}{(4\pi\epsilon_0)^2 r^6} \int_{\nu_1}^{\infty} \alpha_1(i\nu)\alpha_2(i\nu)d\nu \quad (10.21)$$

Note that under such treatment, the vdW interaction is essentially T -independent. Use the approximated form of α , $\alpha(i\nu) = \alpha_0/[1 + (i\nu/\nu_1)^2]$, and $\epsilon_3 = 1$, the integral ends up with:

$$w(\nu > 0, r) = -\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\epsilon_0)^2 r^6} \frac{h\nu_{11}\nu_{12}}{\nu_{11} + \nu_{12}} \quad (10.22)$$

which is finally the London form of dispersion energy.

Now we know why this interaction is called “dispersion”. The largest contribution to the energy in eq 10.21 comes from the range where ν is close to ν_I . Since ν_I is usually in UV range, such interaction is dominated by the polarizabilities from Vis to UV frequencies. As the polarizability and permittivity are closely related to the dispersion of light, it is not hard to understand why it is originally coined as “dispersion interaction”.

10.4 Macroscopic: Lifshitz theory

So far, we have seen how to calculate the vdW interactions by either explicitly use the Keesom, Debye and London interactions, or using the McLachlan equation. All the equations can lead to Hamaker constant. Such theory still has some disadvantages, such as:

1. The many-body effect, i.e. influence of 3 or more bodies is not considered
2. The retardation, i.e. finite time for EM fluctuations to response.
3. Lacking a general form of interaction regardless of geometry

A final solution to this problem is the Lifshitz theory, which consider the macroscopic materials as continuous media, and the molecular polarizability is translated into permittivity. The Lifshitz theory does not consider additivity of vdW interaction, which makes it perfect for calculating macroscopic interactions. In addition, the Lifshitz theory, in its complete form, considers both electrostatic and magnetism, as well as the finite speed of light (Figure 10.6).

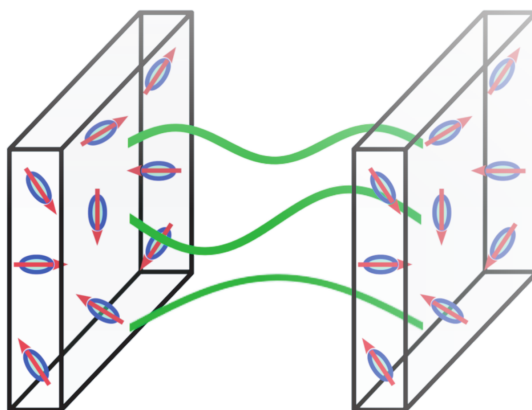


Figure 10.6: Illustration of Lifshitz’s macroscopic theory of van der Waals interactions. The vdW interaction is the result of oscillating fields (green wave-like curves) between 2 macroscopic bodies. Figure adapted from arXiv:1509.03338.

The Lifshitz theory is rather complicated in its original form. We will use a simpler language to explain its basic ideas.

From the McLachlan's model, the Hamaker constant of bulk body 1 and 2 over a medium 3, can be written as:

$$A_{\text{vdW}} = \pi^2 \rho_1 \rho_2 \beta_{132} = \pi^2 \rho_1 \rho_2 \frac{6k_B T}{(4\pi\epsilon_0)^2} \sum_{n=0}^{\infty} \frac{\alpha_1(i\nu_n)\alpha_2(i\nu_n)}{\epsilon_3(i\nu_n)} \quad (10.23)$$

where ρ_1 and ρ_2 are the number densities of species 1 and 2. Now suppose we are treating the materials 1 and 2 as continuous media, the question essentially becomes, how does the polarizability α_1 in its own medium ϵ_1 looks like from another medium ϵ_3 ? We will look into this problem by comparing the micro- and macroscopic approaches of interaction (Figure 10.7).

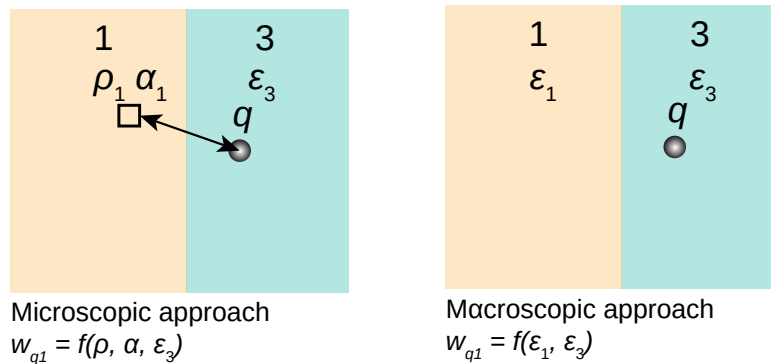


Figure 10.7: Comparison between microscopic and macroscopic approaches calculating the interaction energy between a charge in medium 3 with a bulk material 1. The interaction energy w_{q1} can either be calculated from microscopic approach integrating the charge-induced dipole energy $w_{q\alpha}$, or from macroscopic approach considering permittivity ϵ_1 . Both approaches should yield the same result.

Let's assume that we have a test point charge q in the medium 3. The interaction energy between the test charge q and a molecule in medium 1 is known from Lecture 9:

$$w_{q\alpha} = -\frac{q^2 \alpha_1}{(4\pi\epsilon_0 \epsilon_3)^2 r^4} \quad (10.24)$$

Assume the distance between q and medium is δ . If we sum the integral over medium 1, then the total interaction between q and medium 1 is:

$$w_{q1} = \int_{\delta}^{\infty} dx \int_0^{\infty} w_{q\alpha}(r = \sqrt{(x^2 + y^2)}) \rho_1 (2\pi y) dy \quad (10.25)$$

The integral gives the energy using microscopic approach:

$$w_{q1} = -\frac{\pi q^2 \rho_1 \alpha_1}{(4\pi\epsilon_0 \epsilon_3)^2 \delta} \quad (10.26)$$

On the other hand, we know that the interaction between a charge and a dielectric surface can be calculated using the “method of image”. Let’s consider a general case, where two medium l and r are separated by the line $x = 0$. They have permittivities ϵ_l and ϵ_r , respectively. Now a test charge q is placed at position $(-\delta, 0)$, the total interaction it feels can be simulated by replacing the medium r by a point charge q' at its mirror position, $(\delta, 0)$, as shown in Figure 10.8. We need to solve the quantity of charge q' and the interactions of this system.

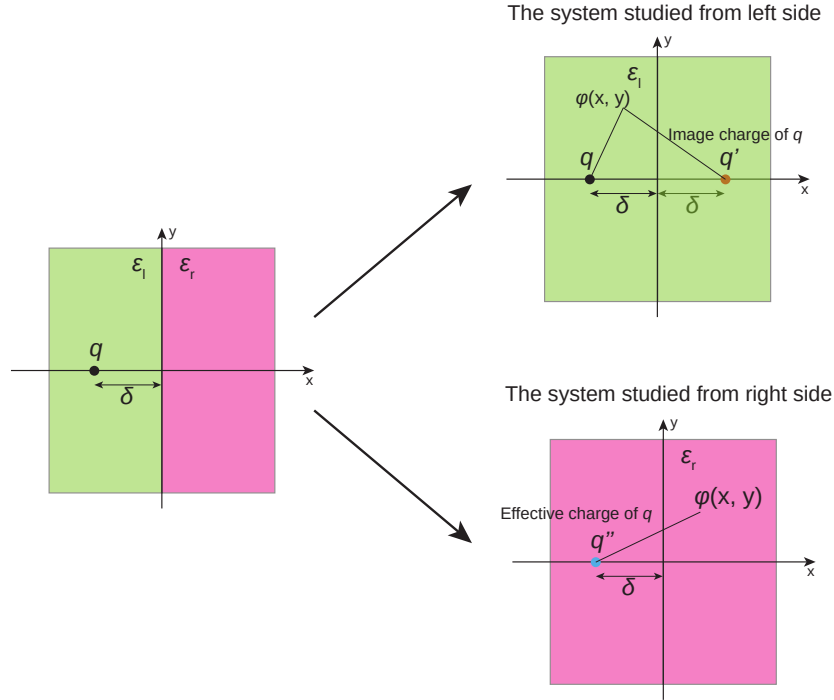


Figure 10.8: Scheme of the method of images.

Left half of space ($x < 0$), the total electrostatic potential is contributed by q and a mirrored image q' located at position $x = \delta$. The total electrostatic potential is thus:

$$\phi(x, y) = \frac{1}{(4\pi\epsilon_0)\epsilon_l} \left[\frac{q}{\sqrt{(\delta + x)^2 + y^2}} + \frac{q'}{\sqrt{(\delta - x)^2 + y^2}} \right], \quad x < 0 \quad (10.27)$$

Right half of space ($x > 0$), the potential seems as if there is a charge q'' at position $x = -\delta$ (because there is no actual image in the right half!). The potential is:

$$\phi(x, y) = \frac{1}{(4\pi\epsilon_0)\epsilon_r} \frac{q''}{\sqrt{(\delta + x)^2 + y^2}}, \quad x > 0 \quad (10.28)$$

The boundary conditions at the interface are:

1. The displacement field is continuous in the x -direction: $D_x^l = D_x^r$ (no boundary charge).

2. The electric field is continuous in the y – direction: $E_y^l = E_y^r$ (energy conservation).

We then have:

$$\begin{aligned} D_x^l &= D_x^r \\ \left. \frac{\partial \phi}{\partial z} \varepsilon_l \right|_{x=0-} &= \left. \frac{\partial \phi}{\partial z} \varepsilon_r \right|_{x=0+} \\ \frac{(q - q')\delta}{\sqrt{(\delta^2 + y^2)^3}} &= \frac{(q'')\delta}{\sqrt{(\delta^2 + y^2)^3}} \end{aligned} \quad (10.29)$$

$$\begin{aligned} E_y^l &= E_y^r \\ \left. \frac{\partial \phi}{\partial y} \right|_{x=0-} &= \left. \frac{\partial \phi}{\partial y} \right|_{x=0+} \\ \frac{(q + q')y}{\varepsilon_l \sqrt{(\delta^2 + y^2)^3}} &= \frac{q''y}{\varepsilon_r \sqrt{(\delta^2 + y^2)^3}} \end{aligned} \quad (10.30)$$

The solution is:

$$q' = -\frac{\varepsilon_r - \varepsilon_l}{\varepsilon_r + \varepsilon_l} q \quad (10.31)$$

$$q'' = \frac{2\varepsilon_r}{\varepsilon_r + \varepsilon_l} q \quad (10.32)$$

This is easy to examine. When the right part medium is a conductor $\varepsilon_r = \infty$, we have $q' = -q$, which is the “image charge” near a metal surface.

Now let’s apply the results from the method of image for interfacial interaction in eq 10.27. Replace $\varepsilon_r = \varepsilon_1$ and $\varepsilon_l = \varepsilon_3$, we get the interaction energy using the macroscopic approach:

$$w_{q1} = w_{qq'} = \frac{qq'}{(4\pi\varepsilon_0)\varepsilon_3(2\delta)} = -\frac{q^2}{(4\pi\varepsilon_0)\varepsilon_3(2\delta)} \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \quad (10.33)$$

Compare this with eq 10.26, we get:

$$\rho_1 \alpha_1 = 2\varepsilon_0 \varepsilon_3 \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \quad (10.34)$$

This is the last piece we need for transforming the microscopic McLachlan theory to the macroscopic Lifshitz theory. Doing the same procedure for $\rho_2 \alpha_2$, and don’t forget the frequency dependency for all ε , we can rewrite eq 10.23 as:

$$A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty} \left[\frac{\varepsilon_1(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_1(i\nu_n) + \varepsilon_3(i\nu_n)} \right] \left[\frac{\varepsilon_2(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_2(i\nu_n) + \varepsilon_3(i\nu_n)} \right] \quad (10.35)$$

There are some properties of the Lifshitz theory:

1. It is dominated by the optical frequencies, like the McLachlan theory.

2. The “Hamaker constant” naturally comes from the difference of dielectric properties between media. When $\epsilon_1 = \epsilon_2 = \epsilon_3$, there will be no dispersion interaction at all.
3. The “Hamaker constant” can be negative! Consider the case where $\epsilon_1 < \epsilon_2 < \epsilon_3$. A nanoscale air bubble will always be repelled from nanoparticles in water.

The Lifshitz theory, in its complete form, consider that the interaction comes from the surface EM modes between interfaces. A general form of the Lifshitz energy in planar geometry can be written as:

$$w(\delta) = \frac{kT}{8\pi l^2} \sum'_{n=0} \int_{2\delta\sqrt{\epsilon(i\nu_n)\mu(i\nu_n)\nu_n/c}}^{\infty} x \ln(\mathcal{D}_E \mathcal{D}_M) dx \quad (10.36)$$

it takes the finite light velocity into account. the \mathcal{D}_E and \mathcal{D}_M are the dispersion relations (specific conditions that surface modes can form) in electrostatic and magnetic fields. The geometric information is embedded in the conditions of \mathcal{D}_E and \mathcal{D}_M . Thus the additive assumption (note we still use it to arrive at eq 10.25) is fully abandoned.

10.5 Limitations of current understanding of vdW interactions

We have seen extensive effort in modeling the vdW interactions in materials. Are we satisfied with the current theoretical framework yet?

The Lifshitz theory is correct from its origin, the electromagnetic fluctuation. However, some assumptions in the Lifshitz theory may be problematic:

1. The abrupt change of dielectric medium is not realistic. In reality we cannot create an interface with step-function-like ϵ profile.
2. The energy divergence problem. We can see that from the Lifshitz theory, the interaction energy when $\delta \rightarrow 0$ will diverge. The step-function-like ϵ profile, causes such discrepancy.
3. ϵ -profile across the interface is not captured. The surface density of molecules varies from its bulk property, as we have seen in the case of water-graphene interface. The uniform ϵ assumption may be problematic.

Again, we should note once we know the exact local ϵ profiles at the interface, the application of Lifshitz theory would be flawless. Two main approaches are used to tackle such problem:

1. Use fluctuation and time-dependent quantum mechanism calculation to calculate interaction of molecular systems.
2. Develop the Lifshitz formulae in non-uniform medium.

References

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